ORGANIC
LETTERS

2003
Vol. 5, No. 9
1535−1538

Synthesis and Characterization of Tricyanovinyl-Capped Oligothiophenes as Low-Band-Gap Organic Materials[†]

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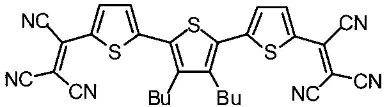
Received February 21, 2003

ABSTRACT



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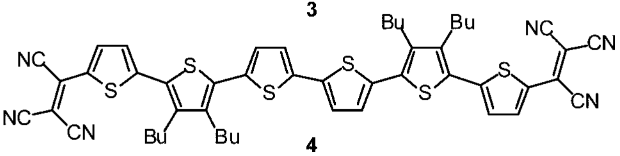

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Tricyanovinyl-capped oligothiophenes of up to six rings have been synthesized and characterized. The substituted oligomers display dramatic reductions in both their optical and electrochemical band gaps in comparison to unsubstituted oligomers. The solvatochromic behavior of the terthiophene-substituted molecule was investigated in a variety of solvents. Stable oxidations and reductions were exhibited by the sexithiophene-substituted molecule on the CV time scale.

Thiophene-based oligomers are an important and promising class of organic materials for their use in organic thin film transistors.[1] These materials are attractive due to their low density, flexibility, and processibility over large coverage areas.[2] The vast majority of oligothiophene-based semiconductors display hole-transporting (p-type) behavior in TFTs.[1,3] More recently, n-type behavior has been achieved in oligothiophenes by the use of perfluoroalkyl[4] or dicyanomethyl[5] capping groups. The n-type behavior of these molecules may be attributed to the stabilization of LUMO orbitals that allow for stable electron injection.

Recently, Bader et al. have shown that oligothiophenes with tricyanovinyl (TCV) substitution are efficient electron acceptors as evidenced by their stable reduction processes.[6] These molecules also exhibit π-stacks in the solid state, which are important for device performance,[7] and they exhibit oxidations at substantially more anodic potentials than their corresponding unsubstituted analogues due to the electron-withdrawing nature of the tricyanovinyl group. It is anticipated that oligomers with α,ω-disubstitution and additional rings (≥ 3) may result in materials with both stable oxidations and reductions. Disubstituted molecules of this type have only been reported for compounds containing up to two rings.[6] To this end, we now report the synthesis and characterization of tricyanovinyl-capped oligothiophenes containing up to six rings.

[†] This paper is dedicated to Professor Larry L. Miller on the occasion of his retirement and his contributions to the field of organic materials.

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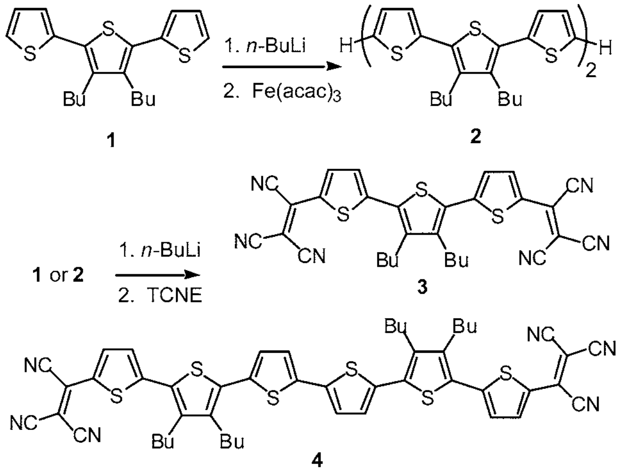
10.1021/ol034317q CCC: $25.00

Scheme 1



The synthesis of unsubstituted and tricyanovinyl-substituted oligomers is outlined in Scheme 1. Dibutylterthiophene[8] **1** was treated with *n*-butyllithium followed by the addition of $Fe(acac)_3$ to form the homocoupled sexithiophene oligomer **2**. The tricyano functionality was introduced in a manner similar to previously reported procedures.[9] Dilithiation of **1** and **2** resulted via the addition of *n*-butyllithium at low temperature. The dianions were subsequently treated with tetracyanoethylene to afford oligomers **3** and **4** in moderate yields.

Although single crystals of **4** have not been obtained, the slow evaporation of a 2:1 acetone/heptane solution gave single crystals of **3** suitable for an X-ray structure determination. The presence of solvent in the crystals decreased the accuracy of the refinement (Supporting Information). The structure consists of two crystallographically independent molecules of **3** and one molecule of acetone in the asymmetric unit. Each molecule adopts a transoid orientation of the sulfur atoms in adjacent thiophene rings. Molecules of **3** are nearly planar as found from a least-squares analysis of all atoms (excluding the butyl groups), which display only 0.153 and 0.115 Å mean deviations from planarity. Furthermore, molecule **3** forms π-stacks along the *a*-axis with an average π-stacking distance of 3.55 Å (Figure 1). This π-stacking behavior is atypical for neutral oligothiophenes but is consistent with thiophene-based molecules possessing one or more electron-withdrawing groups.[4−6,10]

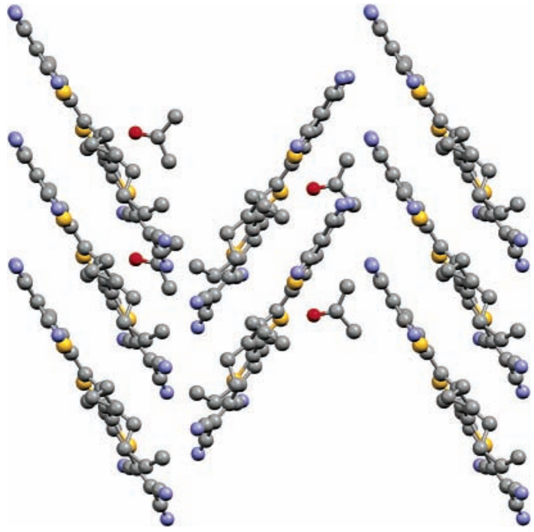


Figure 1. Crystal packing of **3** illustrating the π-stacking of adjacent molecules and location of solvent molecules viewed perpendicular to the *b*-axis (hydrogen atoms omitted).

The electronic spectra of oligomers **1**−**4** were recorded in dichloromethane (Table 1, Figure 2). Each molecule exhibits an intense band attributed to the $\pi-\pi^*$ transition of the conjugated oligothiophene system. Dramatic differences in energy occur upon tricyanovinyl substitution of oligomers **1** and **2**. For example, unsubstituted terthiophene oligomer **1** (λ_{max} = 336 nm) is shifted 247 nm upon tricyanovinyl substitution (oligomer **3**, λ_{max} = 583 nm). A similar, but smaller effect has been observed upon dinitro substitution of **1** (λ_{max} = 444 nm).[10a] This behavior has been attributed to the large stabilization of the LUMO by the electron-withdrawing groups.[11] Dicyano substitution[12] of terthiophene results in λ_{max} = 380 nm. It is evident that

Table 1. Physical Properties of Tricyanovinyl-Capped Oligothiophenes

	electronic spectral data		optical band gap		electrochemical data[c]		
oligomer	solution[a] λ_{max}, nm (ΔE, eV)	thin film[b] λ_{max}, nm (ΔE, eV)	solution, eV	film, eV	oxidation processes. $E°$ (V)	reduction processes, $E°$ (V)	electrochemical band gap, eV
1	336 (3.69)	d	3.15	d	1.11[e]	f	
2	411 (3.02)	430 (2.88)	2.54	2.38	0.81, 0.97, 1.94[e] (n = 2)	f	
3	583 (2.13)	596 (2.08)	1.88	1.73	1.72[e]	−0.36 (n = 2) −1.33[g] (n = 2)	1.84
4	628 (1.97)	699 (1.77)	1.63	1.42	1.04, 1.27	−0.45 (n = 2) −1.13 (n = 2)	1.33

[a] Measured in dry dichloromethane. [b] Reported values are uncorrected ATR values. [c] Potentials vs Ag/AgCl in 0.1 M $TBAPF_6/CH_2Cl_2$ solution. [d] Compound **1** is an oil. [e] Irreversible process; E_{pa} value provided. [f] No observable reduction processes. [g] Irreversible process; E_{pc} value provided.

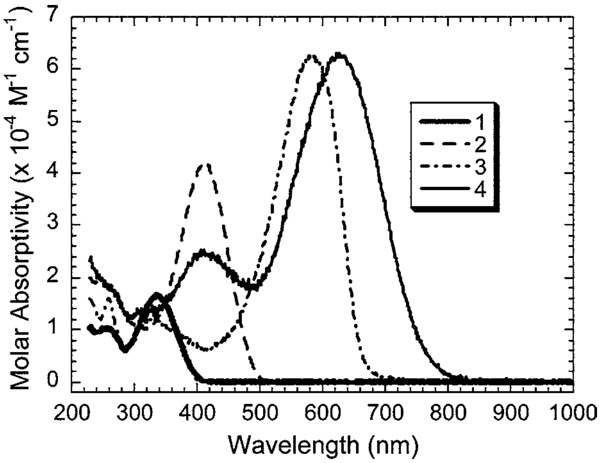


Figure 2. Electronic spectra of oligomers **1**−**4** recorded in dichloromethane.

tricyanovinyl substitution has the most dramatic effect on the energy of the electronic transition in these molecules.

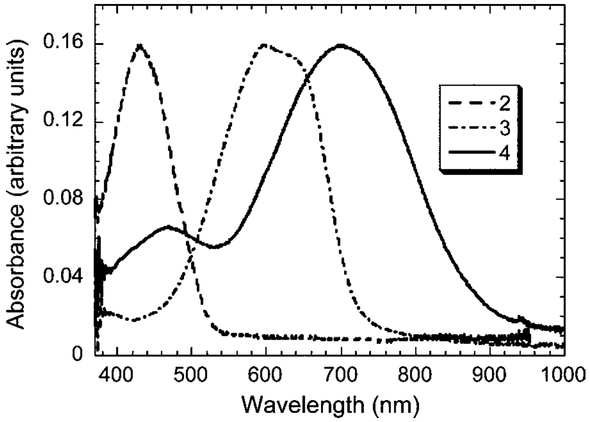


Figure 3. Electronic spectra for thin films of oligomers **2**−**4**.

The electronic spectra of thin films of oligomers **2**−**4** were also recorded. Compound **1** is a room-temperature oil, and its thin film spectrum was not measured. Figure 3 displays the electronic spectra of the oligomers cast from a dichloromethane solution onto a cubic zirconia ATR crystal. As expected, the spectra are red-shifted compared to the solution phase, and this low-energy shift is consistent with solid-state spectra of conjugated homologues and polymers.[13] Optical band gaps (Table 1) were approximated by extrapolation of the low-energy side of the absorption spectra to the baseline as with other oligothiophene co-oligomers.[14]

Tricyanovinyl-substituted hetero-oligomers have been known to demonstrate solvatochromic[15] and vapochromic[16] behavior. The solubility of **3** in a wide variety of solvents warranted a solvatochromic investigation; compound **4** was less soluble and was not studied. The effect of the solvent on the electronic transition for oligomer **3** is outlined in Table 2. The highest energy transitions are found with nonpolar solvents such as hexane and cyclohexane. More polar solvents such as DMSO resulted in lower energy transitions. This behavior has been defined as a positive solvatochromic response ($\Delta\nu = +1640$ cm^{-1})[17] that is related to a greater stabilization of the excited state relative to the ground state with increasing polarity of the solvent. Noteworthy is the behavior of **3** in chlorinated solvents such as chloroform and dichloromethane, which display the lowest energy transitions. Similar behavior has been observed for donor−acceptor molecules of terthiophene where the trend was rationalized as a consequence of an intramolecular charge transfer.[18]

Table 2. Solvatochromic Behavior of Oligomer **3**

solvent[a]	λ_{max} (nm)	ν_{max} (cm^{-1})
hexane	536.4	18 640
cyclohexane	539.8	18 530
diethyl ether	545.0	18 350
ethyl acetate	549.1	18 210
toluene	555.7	18 000
THF	555.7	18 000
acetone	556.4	17 970
benzene	557.1	17 950
2-propanol	559.1	17 890
n-butanol	560.8	17 830
acetonitrile	560.8	17 830
DMF	562.9	17 770
DMSO	585.4	17 080
chloroform	588.2	17 000
dichloromethane	588.2	17 000

[a] Solvents used as received.

The redox properties of all oligomers were investigated by cyclic voltammetry (Table 1). All oligomers displayed

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oxidative processes under the experimental conditions. Terthiophene **1** displays an irreversible oxidation at $E_{pa} = 1.11$ V, characteristic of uncapped terthiophene oligomers. Sexithiophene **2** displays two reversible oxidations with $E°_{1+/0} = 0.81$ V and $E°_{2+/1+} = 0.97$ V with the third and fourth oxidations merged into a single process with $E_{pa} = 1.94$ V. Upon tricyanovinyl substitution, the oligomers display oxidations at more positive potentials as a consequence of the destabilizing effect of the electron-withdrawing TCV groups. For example, oligomer **3** (Figure 4) displays a quasireversible oxidation at $E_{pa} = 1.72$ V, an anodic shift of 0.61 V with respect to the unsubstituted terthiophene. Sexithiophene **4** (Figure 4) displays two reversible oxidations with $E° = 1.04$ and 1.27 V, corresponding to the formation of the cation radical and dication, respectively. Clearly, by increasing the length of the oligothiophene π-system, coupled with α,ω-disubstitution, stable oxidations can be obtained with TCV-oligothiophenes.

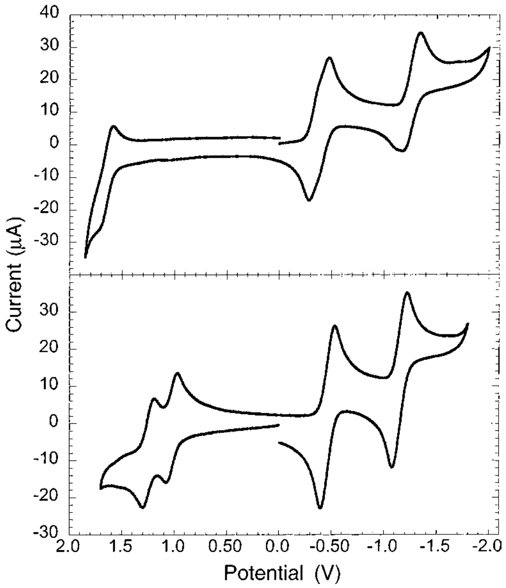

Figure 4. Cyclic voltammograms of **3** (top) and **4** (bottom) in 0.1 M $TBAPF_6/CH_2Cl_2$, $\nu = 100$ mV/s.

In contrast to the unsubstituted oligomers, the TCV-oligomers display reduction processes (Table 1, Figure 4). Both **3** and **4** display stable reductions on the CV time scale, consisting of two pairs of two-electron processes at $E° = -0.36$ and -0.45 V, respectively. The similarity of these potentials suggests that the reductions are mainly TCV centered as previously observed.[6] Electrochemical band gaps (Table 1) were calculated as described previously[19] from the onset potentials of the anodic and cathodic processes and agree well with the calculated optical band gaps. To our knowledge, these are some of the lowest band-gap materials based on aromatic oligothiophenes.

In summary, we have synthesized tricyanovinyl-capped oligothiophenes of up to six rings. These materials exhibit dramatic changes in both their electronic and redox properties in comparison to the unsubstituted materials. The TCV-oligomers display both stable oxidation and reduction processes. This behavior, coupled with their favorable π-stacking features, makes them promising candidates for n-channel or ambipolar semiconductors. Experiments are underway to test this hypothesis.

Acknowledgment. This work was supported by the MRSEC program of the National Science Foundation under Award DMR-0212302.

Supporting Information Available: Experimental procedures, details, and X-ray structure (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

OL034317Q

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